



Research Paper

Case study of a modern lean-burn methane combustion catalyst for automotive applications: What are the deactivation and regeneration mechanisms?



Niko M. Kinnunen ^{a,*}, Janne T. Hirvi ^a, Kauko Kallinen ^b, Teuvo Maunula ^b,
Matthew Keenan ^c, Mika Suvanto ^{a,*}

^a University of Eastern Finland, Department of Chemistry, P.O. Box 111, FI-80101, Joensuu, Finland

^b Dinex Ecocat Oy, Global Catalyst Competence Centre, P.O. Box 20, FI-41331, Vihtavuori, Finland

^c Ricardo UK Ltd, Shoreham Technical Centre, Shoreham-by-Sea, West Sussex, BN43 5FG, United Kingdom

ARTICLE INFO

Article history:

Received 17 October 2016

Received in revised form 15 January 2017

Accepted 5 February 2017

Available online 6 February 2017

Keywords:

Methane
Oxidation
Catalyst
Sulfur
Poisoning
Water
Palladium sulfate

ABSTRACT

One way to lower CO₂ and other harmful emissions of the transportation sector is the development of natural gas fueled vehicles. Availability of natural gas is good, and it is easy to apply to stoichiometric and lean-burn engines, which makes it ready-to-use technology. The main concern in the field is a sulfur poisoning of the exhaust gas after treatment system. We aim to clarify mechanisms of sulfur poisoning and regeneration of a lean-burn methane oxidation catalyst. Overall, it is concluded that sulfur itself is not the only reason for the deactivation of methane oxidation catalyst, but it is a joint effect of water vapor and sulfur species. The irreversible sulfur poisoning deteriorates oxygen mobility and hinders water desorption, which inhibits low temperature methane oxidation activity. The regeneration of sulfur poisoned catalyst takes place stepwise: PdSO₄ → PdSO₃ + 0.5O₂ → Pd + SO₂ + 0.5O₂. The formation of metallic palladium makes the catalyst vulnerable for sintering, which leads to deactivation during long-term regeneration.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

The increased adoption of alternative fuel vehicles will assist in lowering CO₂ emissions of the transportation sector. Natural gas is an alternative fuel which has promising characteristics as a transportation fuel, since its availability is good, and it is easy to apply with present stoichiometric and lean burn engine technology, which makes it a ready-to-use technology. Natural gas contains mainly CH₄, which has over 20 times greater greenhouse gas potential than that of CO₂. Thus, the overall greenhouse gas potential of the vehicle may increase if CH₄ cannot be fully converted in an exhaust gas aftertreatment system. The main concern in the long-term use of natural gas as a fuel in lean-burn engines is the sulfur poisoning of the aftertreatment system. Euro VI and the future emission regulations demands long durability of the catalyst. Durability requirement for heavy-duty aftertreatment systems varies

from 160 000 km (or 5 years) to 700 000 km (or 7 years) depending on the mass of the vehicle [1].

Stoichiometric operating natural gas applications have significantly higher exhaust gas temperatures compared to lean operating natural gas engines. The excess oxygen in the combustion chamber under lean operation leads to lower exhaust gas temperatures. This raises a significant challenge in CH₄ control for lean operating natural gas applications. Hence minimizing deactivation, either thermally or via poisons, will maintain CH₄ control efficiency of the catalyst system which becomes challenging at low temperatures.

After decades of studying, the active phase of low temperature CH₄ combustion catalyst under lean-burn conditions has been concluded to be a mixed Pd-PdO_x phase [2–7] promoted with a small amount of Pt [8,9]. More precisely, PdO(101) surface has been shown to be the main contributor for low temperature activity of the CH₄ oxidation catalyst [10–12]. However, sulfur compounds originated from natural gas and lubricant oils accumulate in the catalyst in long-term use and decrease its low temperature CH₄ conversion activity. The deactivation of the catalyst has been linked to formation of surface PdSO_x or even bulk PdSO₄ regardless of the presence of water vapor [13–15]. The formation of sulfur species can be hindered by using Pt promoter and/or sulfating support

* Corresponding authors.

E-mail addresses: Niko.Kinnunen@uef.fi (N.M. Kinnunen), Mika.Suvanto@uef.fi (M. Suvanto).

Table 1

Catalyst designations, aging treatment and mechanism details.

Sample designation	Treatment	Aging mechanism
Fresh	Calcined in air at 550 °C.	–
HT aged	Hydrothermally aged at 700 °C for 20 h.	Thermal stability of the washcoat.
HT + SO ₂ aged	Hydrothermally aged and sulfur poisoned under wet conditions.	Chemical poisoning of active metal species and washcoat.
4% PdSO ₄ /Al ₂ O ₃	Dried in air at 100 °C.	Reference material for sulfur poisoning, where PdSO ₄ is dispersed over alumina.
Physical mixture of PdSO ₄ and Al ₂ O ₃	Mixed with a spatula.	Bulk PdSO ₄ properties.

material [16,17]. It is also known, that water alone can deactivate the catalyst by forming Pd(OH)₂ [18,19], whereas the joint effect with sulfur species has been proposed to accelerate the formation of inactive sulfur species [13,20].

Regeneration of the methane oxidation catalyst has been studied to recover the low temperature CH₄ conversion activity. Treatment under H₂ gas in a temperature range of 100 °C–600 °C leads to only partial regeneration due to simultaneous sintering of active metal particles and possible formation of PdS [15,21,22]. Regeneration of the catalyst at 600 °C with CH₄ has been observed to recover the low temperature methane conversion activity of the sulfur poisoned catalyst [23,24], completely [25]. The regeneration under nitrogen or in vacuum has been observed to be dependent on temperature and even full recovery can be achieved at 600 °C. The recovery is concluded to follow the Reaction (1) leading to the decomposition of PdSO₄ to active PdO [22].



Our goal is to give an alternative explanation for the joint effect of water and sulfur species on the deactivation of the catalyst, and to highlight the importance of the active metal state during the regeneration without focusing only on recovery in activity. The key research questions are (i) how does sulfur poison the lean-burn methane oxidation catalyst, (ii) how does the catalyst regenerate, and (iii) what is the consequence of repetitive regeneration? Poisoning and regeneration mechanisms will be proposed and discussed for lean-burn methane oxidation catalysts.

2. Experimental

2.1. Catalyst preparation and treatments

Catalysts were prepared by coating metal substrates using conventional preparation methods [24]. The coated catalysts in this study were provided by Dinex Ecocat Oy. A catalyst slurry was prepared by mixing alumina based raw materials into de-ionized water in a beaker. The homogenization and size distribution of raw material particles in the slurry was adjusted by milling. Palladium and platinum precursors were added into the slurry resulting in the Pt/Pd weight ratio of 1:4. The total noble metal loading in each catalyst was 7.06 g l⁻¹. The catalyst coatings were added on oxidation resistant metal alloy foils by an open foil coating method. The cell density of the substrate was 400 cells per in². After wet coating, the samples were dried at 150 °C and calcined in air at 550 °C for 3 h. The corresponding catalyst is designated as fresh in Table 1.

All aging treatments (see Table 1) were carried out under excess of oxygen. The exact gas mixtures are tabulated in Table 2. Hydrothermal treatment (HT) was done at 700 °C for 20 h to the monolith catalyst by mixing 10% water vapor into air giving oxygen content of 18.9%. A gas hourly space velocity (GHSV) of 4000 h⁻¹ was applied in the hydrothermal aging. The sulfur poisoned catalyst (HT + SO₂ aged) was first aged hydrothermally and then treated with a sulfur containing gas of 25 ppm SO₂, 10% O₂, 8% H₂O, and N₂ as a balance for 20 h at 400 °C.

Model powder form catalysts were prepared (see Table 1) to explain and understand the activity and regeneration of the

sulfur poisoned catalyst. To prepare 4% PdSO₄/Al₂O₃ catalyst, alumina (Sasol SBa-200) was used as a support material and PdSO₄ as a palladium precursor (Sigma Aldrich, CAS:13566-03-5). Palladium was impregnated in ion exchanged water over alumina. After 18 h of stirring, water was evaporated at room temperature. Finally, the obtained powder was dried at 100 °C for 2 h. The corresponding physical mixture of PdSO₄ and alumina was prepared by mixing with a spatula.

2.2. Characterization methods

Elemental analysis experiments were carried out with an Elementar varioMICRO cube device. Calibration was carried out by using sulfanilamide, and during the measurements sulfamethazine was used as a reference compound for sulfur. The mass of the sample was 10 mg in the measurement.

Surface areas of the catalysts were measured with a Quantacrome Autosorb-iQ. Sample weight of 100 mg was used for the measurement. The measurement was carried out at –196 °C under liquid nitrogen. Prior to measurement each sample was heated under vacuum at 350 °C for 120 min to remove residuals of air and moisture.

Powder X-ray measurements were carried out in order to determine PdO crystallite size by Bruker-AXD D8 Advance device with Cu K α radiation source. The diffraction pattern was recorded with a scanning speed of 0.11° min⁻¹ varying 2 θ value from 15° to 85°. A step size of 0.02° was used.

The chemical state of the noble metal was studied with temperature programmed oxidation (TPO) hysteresis technique. A sample of 100 mg was heated from room temperature to 1000 °C with a heating rate of 10 °C min⁻¹ under continuous flow of 10% O₂/He blend gas. Cooling down to 250 °C with the same rate followed the heating phase. The gas flow rate was 20 ml min⁻¹. The hysteresis cycle was repeated three times for the fresh and HT aged catalysts, and four times for the HT + SO₂ aged catalyst to reach stable hysteresis. No pretreatment was done prior to the measurement and a cold trap was not used in the measurement.

Light-off tests of the fresh, HT aged, and HT + SO₂ aged catalysts were performed with a laboratory scale micro reactor system. Monolith samples with a length of 18 mm and diameter of 10 mm were used in the experiments. A gas flow rate of 1180 ml min⁻¹ was used giving a gas hourly space velocity of 50 000 h⁻¹. Simulated exhaust gas (Table 2) was mixed with Brooks (GF-series) gas mass flow controllers and water was fed to the gas stream at 100 °C with a high pressure pump. In the experiment simulated exhaust gas mixture was flowed through a monolith catalyst and the product gas was analyzed with a Gasmet™ FTIR gas analyzer, designed for exhaust gas applications. The gas composition was analyzed with an interval of 20 s by using 5 s scan time. The exhaust gas was kept all the time at 180 °C with heated gas lines in order to avoid condensation. The temperature of the catalyst was recorded inside the reactor precisely above the monolith. The catalyst temperature was increased with a rate of 7 °C min⁻¹ during light-off test.

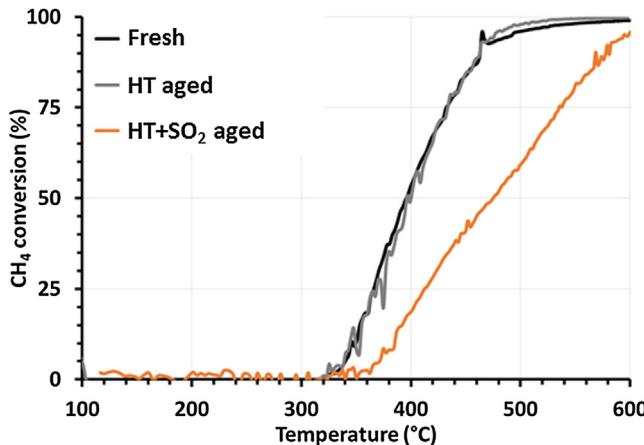
Steady-state activity of the HT + SO₂ aged catalyst during the regeneration was measured at 500 °C. The regeneration was carried out by decreasing the oxygen concentration of the exhaust gas

Table 2

Aging and simulated exhaust gas mixtures, and gas hourly space velocities.

	HT aging	HT + SO ₂ aging	Simulated exhaust gas	Simulated exhaust gas without water
CH ₄	–	–	2000 ppm	2000 ppm
C ₃ H ₈	–	–	500 ppm	500 ppm
CO	–	–	2000 ppm	2000 ppm
NO	–	–	500 ppm	500 ppm
SO ₂	–	25 ppm	10 ppm	10 ppm
CO ₂	–	–	6%	6%
O ₂	18.9%	8%	10%	10%
H ₂ O	10%	10%	10–12%	–
N ₂	Bal.	Bal.	Bal.	Bal.
GHSV	4000 h ^{–1}	4000 h ^{–1}	50 000 h ^{–1}	50 000 h ^{–1}

Gases were supplied by AGA.

**Fig. 1.** Methane conversion curves of the fresh, HT aged, and HT + SO₂ aged catalysts with simulated exhaust gas.

stepwise from 10% down to 0.18%. The decrease in oxygen concentration was compensated with nitrogen gas to maintain the gas hourly space velocity over the catalyst.

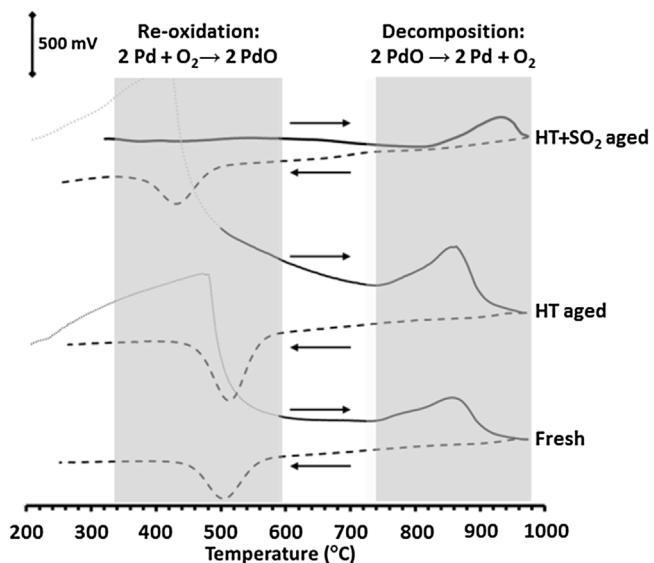
3. Results and discussion

3.1. Catalyst state and activity

Sulfur contents, BET surface areas, and PdO crystallite sizes of the catalysts are shown in **Table 3**. The sulfur poisoning results, for sulfur content of 0.97 wt.-%, of the HT + SO₂ catalyst, originated from both palladium and aluminum based sulfur species. Sulfur content of 0.88 wt.-% corresponded well with the theoretical value of 4% PdSO₄ loading over alumina support. Hydrothermal aging and sulfur poisoning decreased the BET surface area slightly compared to the fresh catalyst. Only a small increase in PdO crystallite size was observed due to aging.

The methane oxidation catalyst suffered sulfur poisoning during long-term operation. The sulfur poisoning issue is demonstrated in **Fig. 1**, under conditions with a realistic gas mixture including water. Methane can be converted completely with the fresh catalyst above 500 °C and 90% conversion can be achieved at 460 °C. Hydrothermal aging did not deteriorate methane oxidation activity. However, after sulfur poisoning, activity of the catalyst decreased remarkably; 90% conversion was reached only at 580 °C. Note also clearly more gradual slope of the HT + SO₂ aged catalyst compared to the fresh and HT aged catalysts.

TPO experiments were carried out in order to study oxygen release and re-oxidation of the fresh, HT aged, and HT + SO₂ aged catalysts (**Fig. 2**). An upward peak shows the thermal decomposition of PdO phase, whereas a downward peak corresponds to the re-oxidation of metallic phase. Evolution of SO₂ due to the

**Fig. 2.** Oxygen release from the fresh, HT aged, and HT + SO₂ aged catalysts during heating is presented as solid lines. Re-oxidation of the metallic phase during cooling is illustrated as dashed lines.

decomposition of sulfur species will be discussed later. The thermal decomposition of PdO phase of the fresh catalyst appeared at a slightly higher temperature than reported previously [9]. The hydrothermal aging did not have a clear effect either on the decomposition temperature of PdO phase nor re-oxidation temperature of the metallic phase. However, sulfur poisoning stabilized the PdO phase during heating and prevents re-oxidation of the metallic phase during cooling i.e. it stabilizes the existing phase. Overall, the result was a wider hysteresis of the sulfur poisoned catalyst.

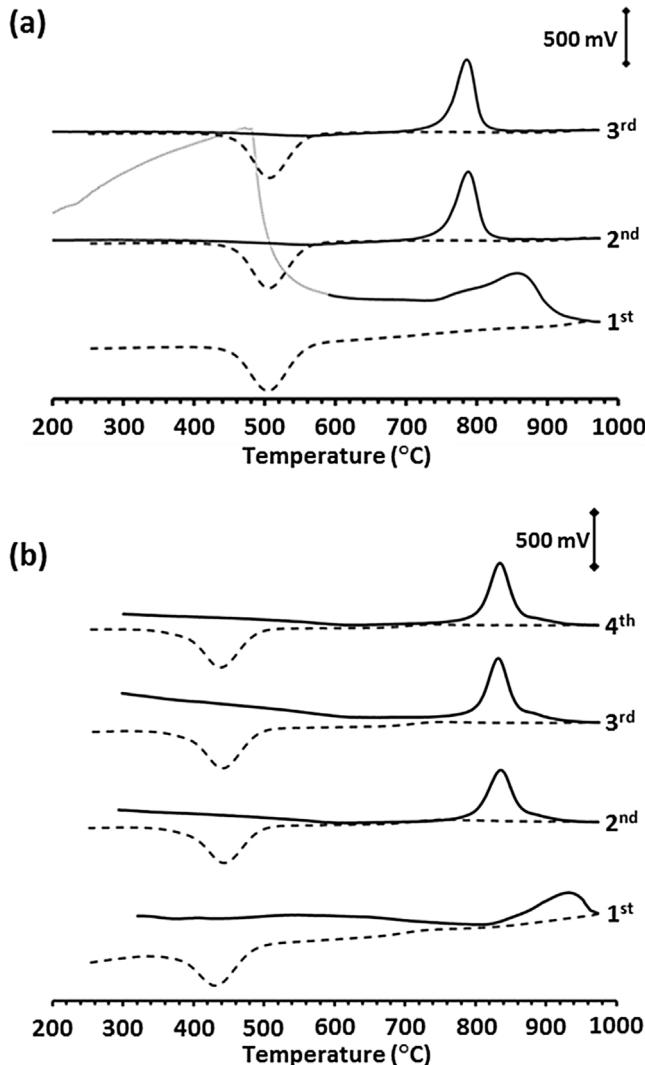
Repeated TPO experiments were carried out to study more closely whether the sulfur poisoning induced change in chemical state of the active metal phase was reversible or not. The repeated TPO results for the fresh and HT + SO₂ aged catalysts are presented in **Fig. 3(a)** and (b), respectively. For the HT aged catalyst, peak positions in the TPO curves were identical compared to the fresh catalyst. As can be seen in **Fig. 3(a)**, the upward peak of the fresh catalyst moved to a lower temperature in the second heating cycle and stabilizes to that position. The peak shift was well in line with the observations of Person et al. [26], who noticed that a small amount of platinum promoted the destabilization of PdO phase. They calcined Pt-Pd/Al₂O₃ catalyst at 1000 °C under air, which was similar to the conditions at the end of heating cycle in our TPO experiments. No shift was seen in the position of downward peak of the fresh catalyst between the repeated TPO measurements, and hence, the overall hysteresis was narrower.

The PdO decomposition peak of the HT + SO₂ aged catalyst moves also to a lower temperature after repeated TPO experiments,

Table 3

Sulfur content, BET surface area, and PdO crystallite size of the catalysts.

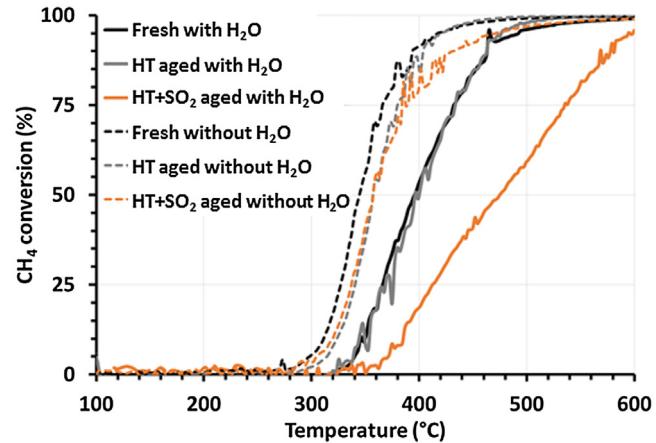
Sample	Sulfur content (wt.-%)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	PdO crystallite size (nm)
Fresh	0	216	1.6
HT aged	0	190	2.1
HT + SO_2 aged	0.97	180	2.7
4% $\text{PdSO}_4/\text{Al}_2\text{O}_3$	0.88	–	Not detected

**Fig. 3.** Oxygen release from (a) the fresh and (b) $\text{HT} + \text{SO}_2$ aged catalysts during heating in repeated TPO experiments are presented as solid lines. Re-oxidation of the metallic phase during cooling is illustrated as dashed lines.

but it does not shift to the same temperature as for the fresh catalyst. Note that a release of a small amount of SO_2 gas, originated from the decomposition of PdSO_4 , was observed only at higher temperatures with quadrupole mass spectrometer. Moreover, the downward peak shifts to higher temperatures. The peaks settled down after third TPO cycle. Even though both peaks moved toward each other's, the overall hysteresis was still wider than that of the fresh catalyst. It means that sulfur had an irreversible chemical effect on active metal phase of the methane oxidation catalyst.

3.2. Sulfur poisoning mechanism

The presence of active Pd-PdO sites is needed for low temperature CH_4 combustion. As shown in the previous study, methane

**Fig. 4.** Methane conversion curves of the fresh, HT aged, and $\text{HT} + \text{SO}_2$ aged catalysts with and without water vapor in the exhaust gas stream.

dissociates over the Pd-PdO catalyst forming methyl and hydroxyl groups [4]. It has been concluded that surface oxygen should be mobile to enable removal of hydroxyl groups in form of water and refill of vacancies by oxygen dissociation [27–29]. Based on our TPO results, however, sulfur poisoning stabilizes structural oxygen and makes it less mobile, while water in the exhaust gas further stabilizes inactive $\text{Pd}(\text{OH})_2$ form of the catalyst [18,19,30]. The joint effect of sulfur poisoning and water is clearly shown above in Fig. 1. Nevertheless, if water vapor is removed from the exhaust gas stream, the performance of the sulfur poisoned catalyst is comparable even to the fresh catalyst (Fig. 4).

According to the results in Fig. 4, the next hypothesis can be done: “*Sulfur does not poison the methane oxidation catalyst, instead it makes the catalyst more sensitive to water vapor poisoning.*” To confirm the statement, the activity of the model powder 4% $\text{PdSO}_4/\text{Al}_2\text{O}_3$ catalyst was measured under simulated exhaust gas with and without water vapor (Fig. 5). The results are compared with the $\text{HT} + \text{SO}_2$ aged catalyst under the similar conditions. It can be seen that the 4% $\text{PdSO}_4/\text{Al}_2\text{O}_3$ catalyst was actually active at low temperature if water vapor is not present, whereas even momentary addition of water decreased its activity notably. So, the previously observed acceleration in the formation of PdSO_4 in the presence of water [13] does not deteriorate the catalyst performance completely. Overall, behavior of the 4% $\text{PdSO}_4/\text{Al}_2\text{O}_3$ catalyst in the low temperature methane oxidation mimics the performance of the $\text{HT} + \text{SO}_2$ aged catalyst. Thus we conclude that less mobile oxygen after sulfur poisoning leads to higher temperature needed for removal of surface hydroxyl groups via water desorption. The effect is pronounced when water vapor is present in the exhaust gas stabilizing the surface hydroxyl groups. The presence of water vapor also pronounces the site blocking effect by molecular water, which is concluded to be one limiting factor for the reaction rate of the catalyst at low temperature [27].

3.3. Regeneration mechanism

Thermal decomposition of the model powder 4% $\text{PdSO}_4/\text{Al}_2\text{O}_3$ catalyst and physical mixture of PdSO_4 and Al_2O_3 were measured

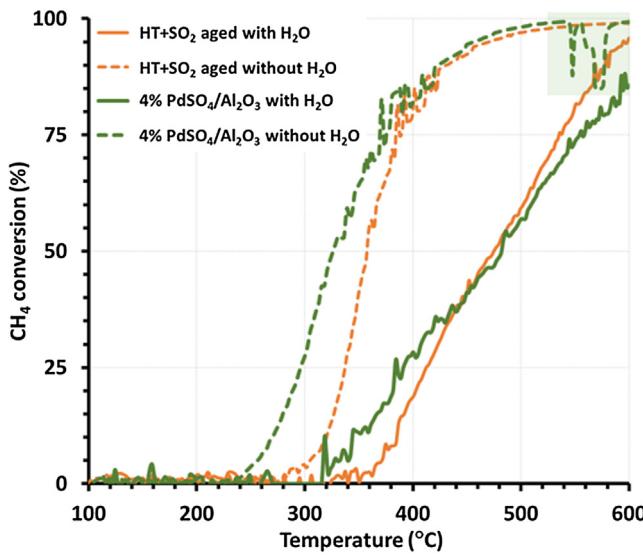
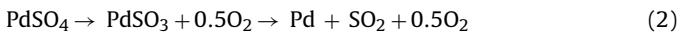


Fig. 5. Methane conversion of the HT + SO₂ aged and 4% PdSO₄/Al₂O₃ catalysts with and without water. The effect of two momentary additions of water vapor into the gas stream for the 4% PdSO₄/Al₂O₃ catalyst is shown in the highlighted area.

to understand the decomposition of the sulfur poisoned catalyst (Fig. 6). The presence of Al₂(SO₄)₃ is not likely. In both cases the first peak corresponded to oxygen release, followed by simultaneous release of oxygen and SO₂ over a wide temperature range. The release of SO₂ was observed at the same temperatures as that for the HT + SO₂ aged catalyst. The results indicate that PdSO₄ decomposes under real operation conditions stepwise via Reaction (2) leading to metallic palladium, instead of palladium oxide as proposed in the Reaction (1). The Reaction (1) would be valid only if an additional peak, due to the decomposition of PdO, would be detected after SO₂ release, which however, is not realistic at high temperatures. Existence of PdSO₃ under low O₂ pressures has been observed in the recent studies as well, thus supporting our conclusion [31].



The decomposition of PdSO₄ to metallic palladium under regeneration conditions can be expected to decrease the CH₄ conversion activity of the catalyst. Fig. 7 shows the CH₄ conversion for the

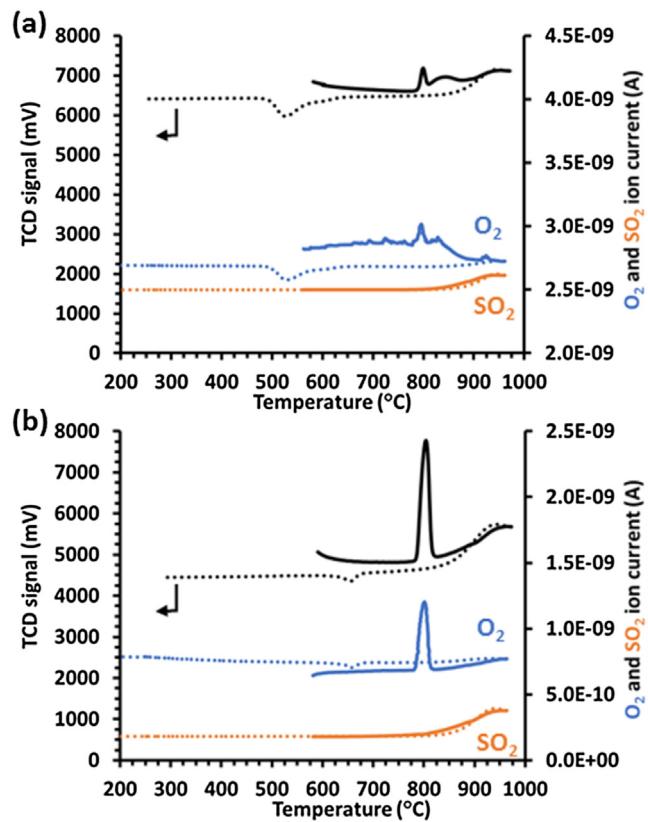


Fig. 6. Thermal decomposition curves of (a) 4% PdSO₄/Al₂O₃ and (b) physical mixture of PdSO₄ and Al₂O₃.

HT + SO₂ aged catalyst as a function of time under steady-state conditions at 500 °C with simulated exhaust gas. Oxygen concentration was decreased in the experiment stepwise from 10% to 0.18% to observe SO₂ release and regeneration of the catalyst due to the decomposition of sulfate species, mainly PdSO₄. The peak value of SO₂ was seen immediately after decrease in oxygen concentration, but the release continued decaying as a function of time. Simultaneously with SO₂ release, CH₄ conversion activity decreased due to the formation of metallic palladium. Metallic palladium is known

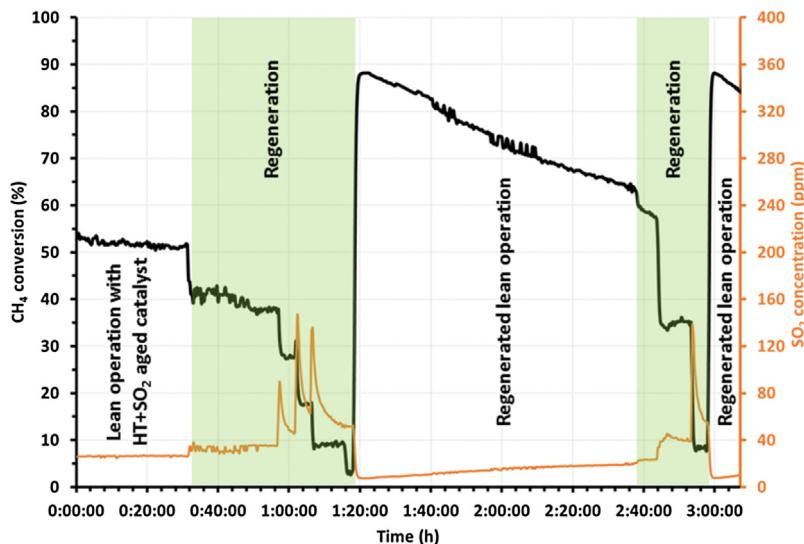


Fig. 7. Regeneration of the HT + SO₂ aged catalyst under steady-state conditions at 500 °C. A black line indicates CH₄ conversion (%), whereas SO₂ concentration (ppm) is shown with an orange line.

to be sensitive for sintering [32–34] and hence a long regeneration period may lead to permanent loss in activity. Finally, when original oxygen concentration level was restored, metallic palladium, originating from the decomposition of PdSO_4 , re-oxidized and the activity was improved temporarily.

4. Conclusions

The study demonstrates the differences in chemical state of noble metal of the fresh, hydrothermally aged, and sulfur poisoned catalysts. The sulfur poisoned catalyst is more sensitive to water inhibition compared to the fresh or hydrothermally aged catalysts. Sulfur poisoning deteriorates oxygen mobility and hinders water desorption, which inhibits low temperature methane oxidation activity of the sulfur poisoned catalyst. The change in chemical state of the active metal is irreversible and cannot be recovered completely after sulfur poisoning. The sulfur poisoned catalyst can be regenerated in two steps: PdSO_4 decomposes to PdSO_3 releasing oxygen, which is followed by simultaneous release of oxygen and SO_2 at wide temperature range. The decomposition of PdSO_4 results, however, metallic palladium, which is inactive in methane combustion. The formation of metallic palladium, especially at high temperatures, may expose the catalyst to sintering and thus permanent decrease in low temperature CH_4 oxidation activity.

The ability to regain methane activity via a regeneration mechanism is crucial for automotive applications. After fully understanding the conditions the catalyst requires for regeneration, the engine and exhaust control strategy of the automotive application can provide these conditions. The temperature and exhaust gas composition can be periodically changed to allow catalyst regeneration to take place with minimal impact on fuel penalty.

Acknowledgements

The research leading to these results has received funding from the *European Union's Horizon 2020 research and innovation programme* under Grant Agreement no. 653391 (HDGAS-project). Laboratory technician Taina Nivajärvi is thanked to taking care the elemental analysis experiments. Laboratory technicians Martti Lapalainen and Urpo Ratinen are acknowledged their expertise and guidance in building of the reactor system for activity tests. Sasol and Dr. Frank Alber is thanked for the providing alumina raw material of model catalyst.

References

- [1] REGULATION (EC) No 595/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL.
- [2] M. Lyubovsky, L. Pfefferle, *Appl. Catal. A-Gen.* 173 (1998) 107–119.
- [3] S. Yang, A. Maroto-Valiente, M. Benito-Gonzalez, I. Rodriguez-Ramos, A. Guerrero-Ruiz, *Appl. Catal. B-Environ.* 28 (2000) 223–233.
- [4] K. Fujimoto, F.H. Ribeiro, M. Avalos-Borja, E. Iglesia, *J. Catal.* 179 (1998) 431–442.
- [5] D. Bounechada, G. Groppi, P. Forzatti, K. Kallinen, T. Kinnunen, *Appl. Catal. B-Environ.* 119–120 (2012) 91–99.
- [6] N.M. Kinnunen, J.T. Hirvi, T. Venäläinen, M. Suvanto, T.A. Pakkanen, *Appl. Catal. A-Gen.* 397 (2011) 54–61.
- [7] N.M. Kinnunen, J.T. Hirvi, M. Suvanto, T.A. Pakkanen, *J. Mol. Catal. A-Chem.* 356 (2012) 20–28.
- [8] L.S. Escandón, S. Ordóñez, A. Vega, F.V. Díez, *Chemosphere* 58 (2005) 9–17.
- [9] G. Lapisardi, L. Urfels, P. Gélin, M. Primet, A. Kaddouri, E. Garbowski, S. Toppi, E. Tena, *Catal. Today* 117 (2006) 564–568.
- [10] A. Antony, A. Asthagiri, J.F. Weaver, *J. Chem. Phys.* 139 (2013) 104702.
- [11] N.M. Martin, d.B. Van, A. Hellman, H. Grönbeck, C. Hakanoglu, J. Gustafson, S. Blomberg, N. Johansson, Z. Liu, S. Axnanda, J.F. Weaver, E. Lundgren, *ACS Catal.* 4 (2014) 3330–3334.
- [12] A. Hellman, A. Resta, N.M. Martin, J. Gustafson, A. Trinchero, P. Carlsson, O. Balmes, R. Felici, R. van Rijn, J.W.M. Frenken, J.N. Andersen, E. Lundgren, H. Grönbeck, *J. Phys. Chem. Lett.* 3 (2012) 678–682.
- [13] D.L. Mowery, R.L. McCormick, *Appl. Catal. B-Environ.* 34 (2001) 287–297.
- [14] P. Gélin, L. Urfels, M. Primet, E. Tena, *Catal. Today* 83 (2003) 45–57.
- [15] T. Yu, H. Shaw, *Appl. Catal. B-Environ.* 18 (1998) 105–114.
- [16] J.K. Lampert, M.S. Kazi, R.J. Farrauto, *Appl. Catal. B-Environ.* 14 (1997) 211–223.
- [17] G. Corro, C. Cano, J.L.G. Fierro, *J. Mol. Catal. A-Chem.* 315 (2010) 35–42.
- [18] R. Burch, F.J. Urbano, P.K. Loader, *Appl. Catal. A-Gen.* 123 (1995) 173–184.
- [19] D. Roth, P. Gélin, M. Primet, E. Tena, *Appl. Catal. A-Gen.* 203 (2000) 37–45.
- [20] D.L. Mowery, M.S. Graboski, T.R. Ohno, R.L. McCormick, *Appl. Catal. B-Environ.* 21 (1999) 157–169.
- [21] J.M. Jones, V.A. Dupont, R. Brydson, D.J. Fullerton, N.S. Nasri, A.B. Ross, A.V.K. Westwood, *Catal. Today* 81 (2003) 589–601.
- [22] L.J. Hoyos, H. Praliaud, M. Primet, *Appl. Catal. A-Gen.* 98 (1993) 125–138.
- [23] F. Arosio, S. Colussi, G. Groppi, A. Trovarelli, *Catal. Today* 117 (2006) 569–576.
- [24] N. Kinnunen, T. Kinnunen, K. Kallinen, SAE technical paper 2013-24-0155 (2013), <http://dx.doi.org/10.4271/2013-24-0155>.
- [25] F. Arosio, S. Colussi, A. Trovarelli, G. Groppi, *Appl. Catal. B-Environ.* 80 (2008) 335–342.
- [26] K. Persson, A. Ersson, K. Jansson, J.L.G. Fierro, S.G. Järås, *J. Catal.* 243 (2006) 14–24.
- [27] M.V. Bossche, H. Grönbeck, *J. Am. Chem. Soc.* 137 (2015) 12035–12044.
- [28] D. Ciuparu, L. Pfefferle, *Catal. Today* 77 (2002) 167–179.
- [29] J. Au-Yeung, K. Chen, A.T. Bell, E. Iglesia, *J. Catal.* 188 (1999) 132–139.
- [30] D. Ciuparu, E. Perkins, L. Pfefferle, *Appl. Catal. A-Gen.* 263 (2004) 145–153.
- [31] F. Ortloff, J. Bohnau, U. Kramar, F. Graf, T. Kolb, *Appl. Catal. B-Environ.* 182 (2016) 550–561.
- [32] D. Ciuparu, M.R. Lyubovsky, E. Altman, L.D. Pfefferle, A. Datye, *Cataly. Rev.* 44 (2002) 593–649.
- [33] P. Euzen, J. Le Gal, B. Rebours, G. Martin, *Catal. Today* 47 (1999) 19–27.
- [34] J.D. Grunwaldt, N.v. Vegtgen, A. Baiker, *Chem. Commun.* (2017) 4635.